Purity Evaluation of Single-Walled Carbon Nanotubes by use of Near-Infrared Spectroscopy

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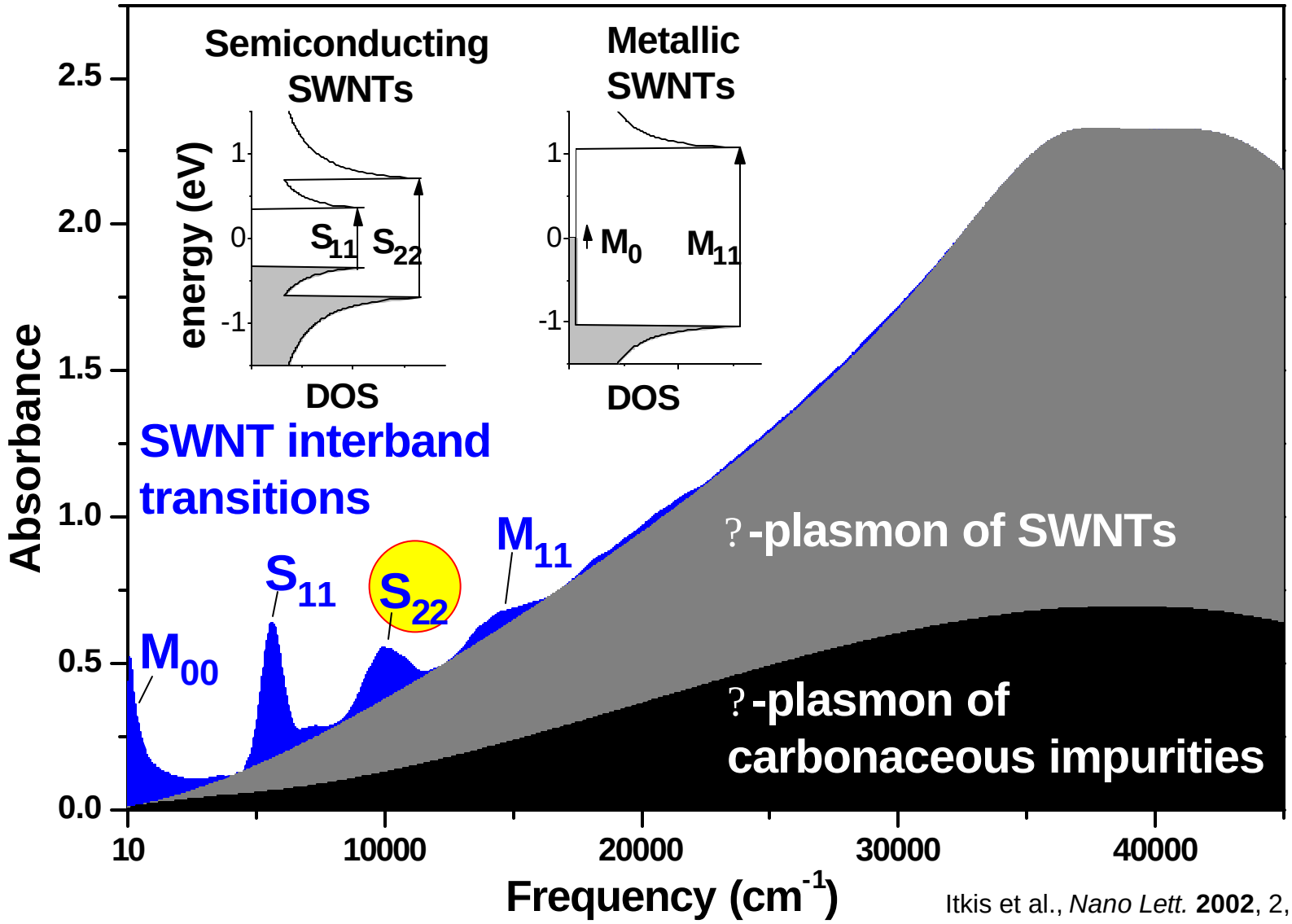
Most popular analytical techniques for SWNT quality evaluation:

- Transmission Electron Microscopy;
- Scanning Electron Microscopy;
- Thermogravimetric Analysis;
- Raman Spectroscopy;
- UV-Visible – Near Infrared Spectroscopy

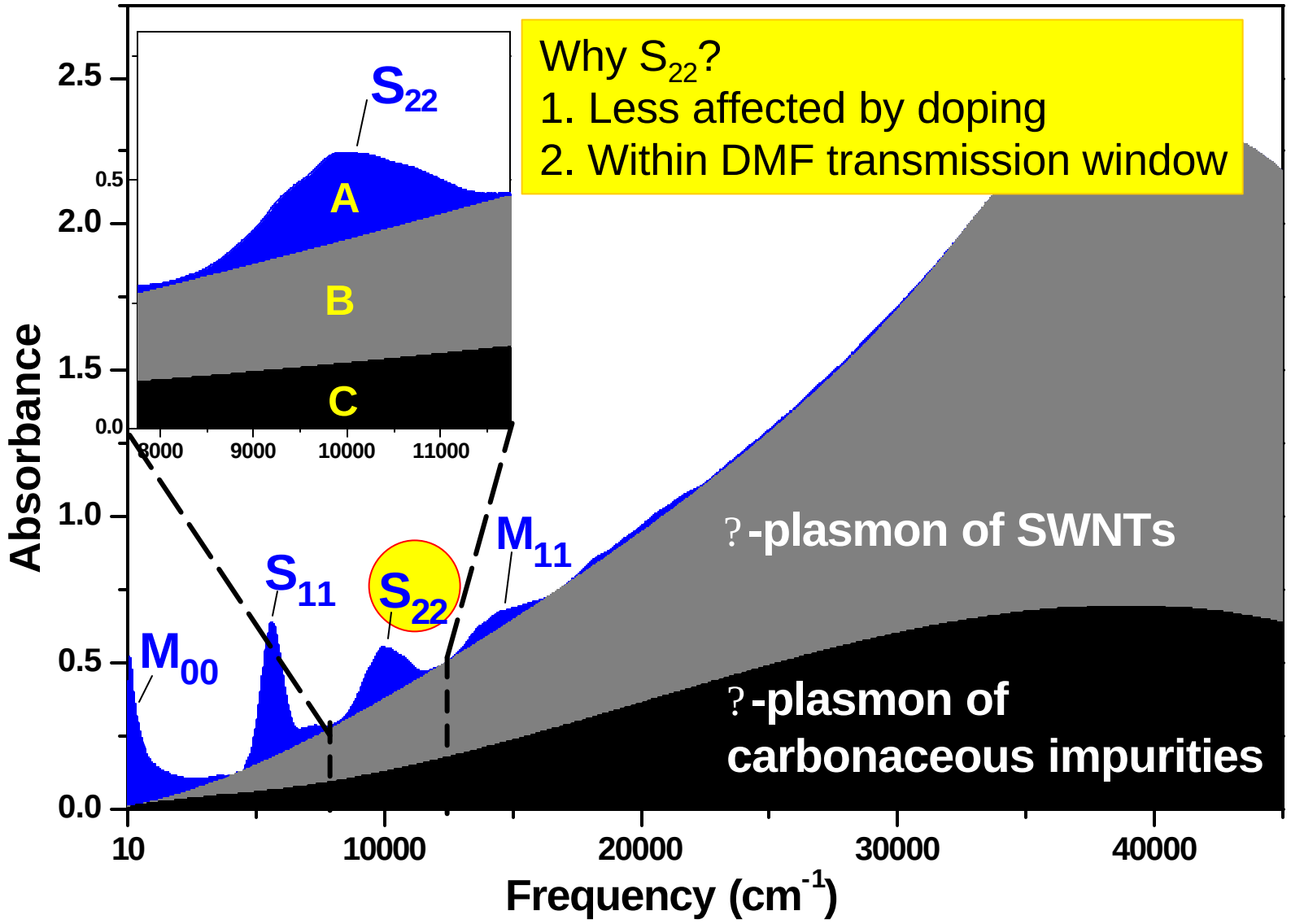
SEM and TEM are valuable techniques, but their application for evaluation of bulk samples (>1g scale) is questionable – less than 10^{-13} g of SWNT material per frame is observable; SWNT soot is very inhomogeneous

DOS and Optical Spectroscopy of SWNTs

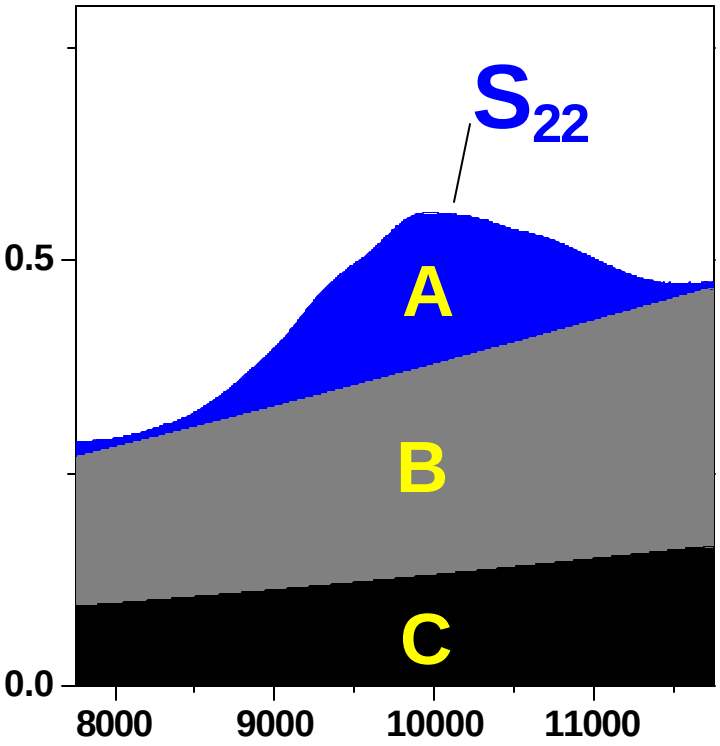


Itkis et al., *Nano Lett.* **2002**, 2, 155
Haddon et al., *MRS Bulletin* **2004**, 29,252

Choose 2nd Semiconducting Interband Transition S_{22}



Purity calculations



A – area of S_{22} interband transition after linear baseline subtraction

T(total area)=A+B+C

PURITY: P ~ A/T

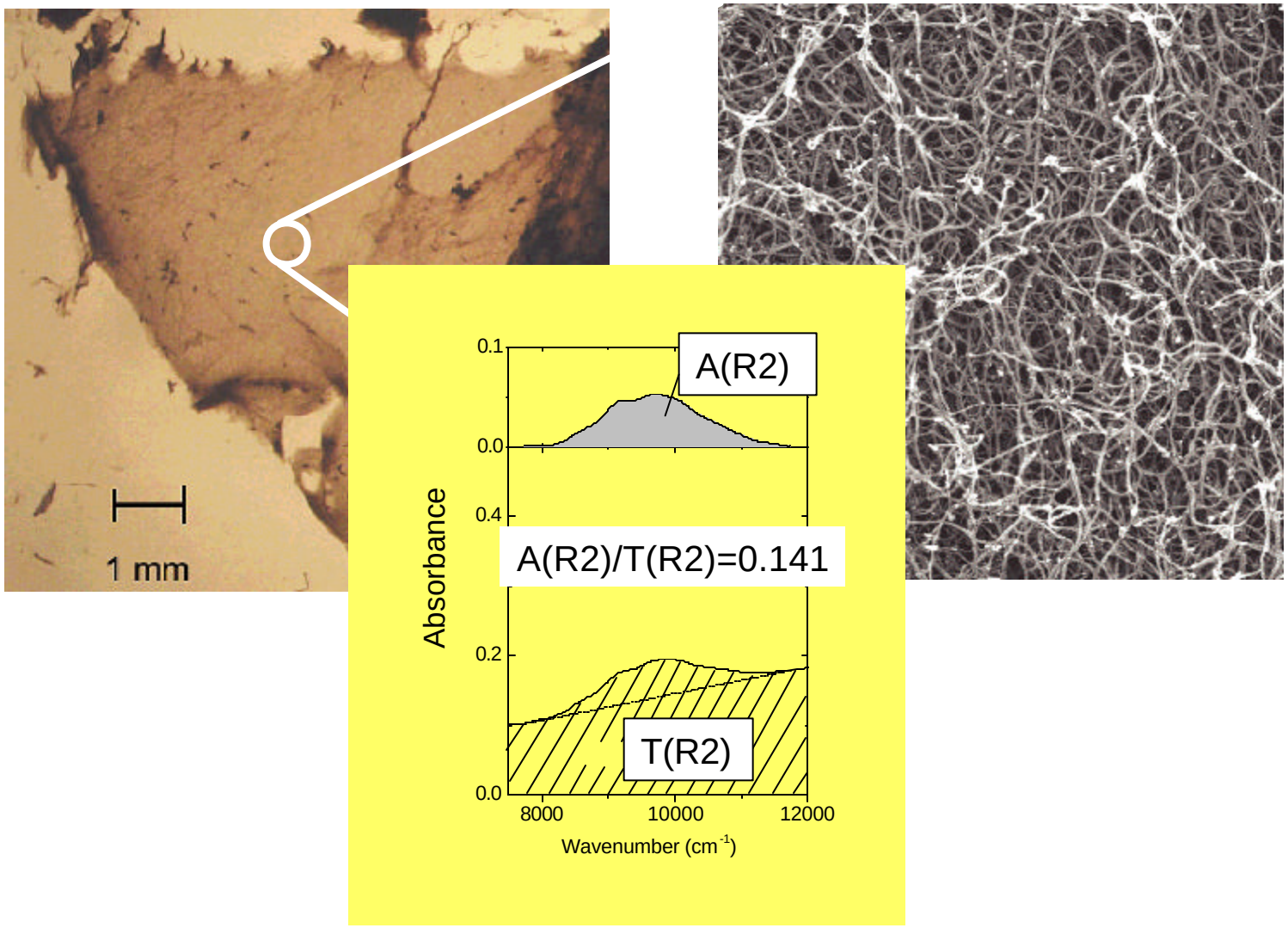
FOR REFERENCE SAMPLE
PURITY: P(R) ~ A (R)/T(R)

$$\text{Relative Purity (RP)} = \frac{(A/T)}{A(R)/T(R)}$$

Spectral cutoff for S_{22}: 7750 – 11750 cm^{-1} (electric arc)

Itkis et al., *Nano Lett.* 2003, **3**, 309
Haddon et al., *MRS Bulletin* 2004, **29**,252

Initial Reference Standard – R2 (high purity raw material)



Itkis, *et al*., *Nano Lett*, **2003**, 3(3), 309-314.

Solution phase or thin film spectroscopy for purity evaluation?

Solution phase spectroscopy:

Chen, J. et al. *Science* **1998**, *282*, 95-98.
Chen, J. et al. *J. Phys. Chem. B* **2001**, *105*, 2525-2528.
Niyogi, S. et al. *Acc. Chem. Res.* **2002**, *35*, 1105-1113.
Bachilo, S. M. et al. *Science* **2002**, *298*, 2361-2366.
Strano, M. S. et al. *Science* **2003**, *301*, 1519-1522.

Thin films spectroscopy:

Kataura H et al, *Synth. Met.* **1999**, *103*, 2555-2558
Petit, P. et al., *Chem. Phys. Lett.* **1999**, *305*, 370-374
Itkis, M. E et al, *NanoLett.* **2002**, *2*, 155-159
Hennrich, F. et al. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2273-2277
Hamon, M. A. et al. *J. Am. Chem. Soc.* **2001**, *123*, 11292-11293.
Wu, Z. et al. *Science* **2004**, *305*, 1273-1276
Kazaoui, S. et al. *Phys. Rev. B* **1999**, *60*, 13339-13342.
Kazaoui, S. et al. *App. Phys. Lett.* **2001**, *78*, 3433-3435.
Hennrich, F. et al.*Phys. Chem. Chem. Phys.* **2003**, *5*, 178-183.
Kamaras, K. et al. *Science* **2003**, *301*, 1501.
Hu, H. et al. *J. Am. Chem. Soc.* **2003**, *125*, 14893-14900.
Jost, O. et al. J. *App. Phys. Lett.* **1999**, *75*, 2217-2219.
Jost, O. et al. *J. Phys. Chem. B* **2002**, *106*, 2875-2883.
Sen, R. et al. *Chem. Mater.* **2003**, *15*, 4273-4279.

Solution phase NIR spectroscopy generates more reliable and reproducible results for purity evaluation

Practical motivation:

- Find optimum parameters for bulk arc-discharge synthesis
- Develop efficient purification procedures

Sample preparation protocol

Sample homogenization:

1st step: 10 g batch – prepare fine dry powder;

2nd step: 50mg of powder – 100 ml DMF, ultrasonication + stirring;

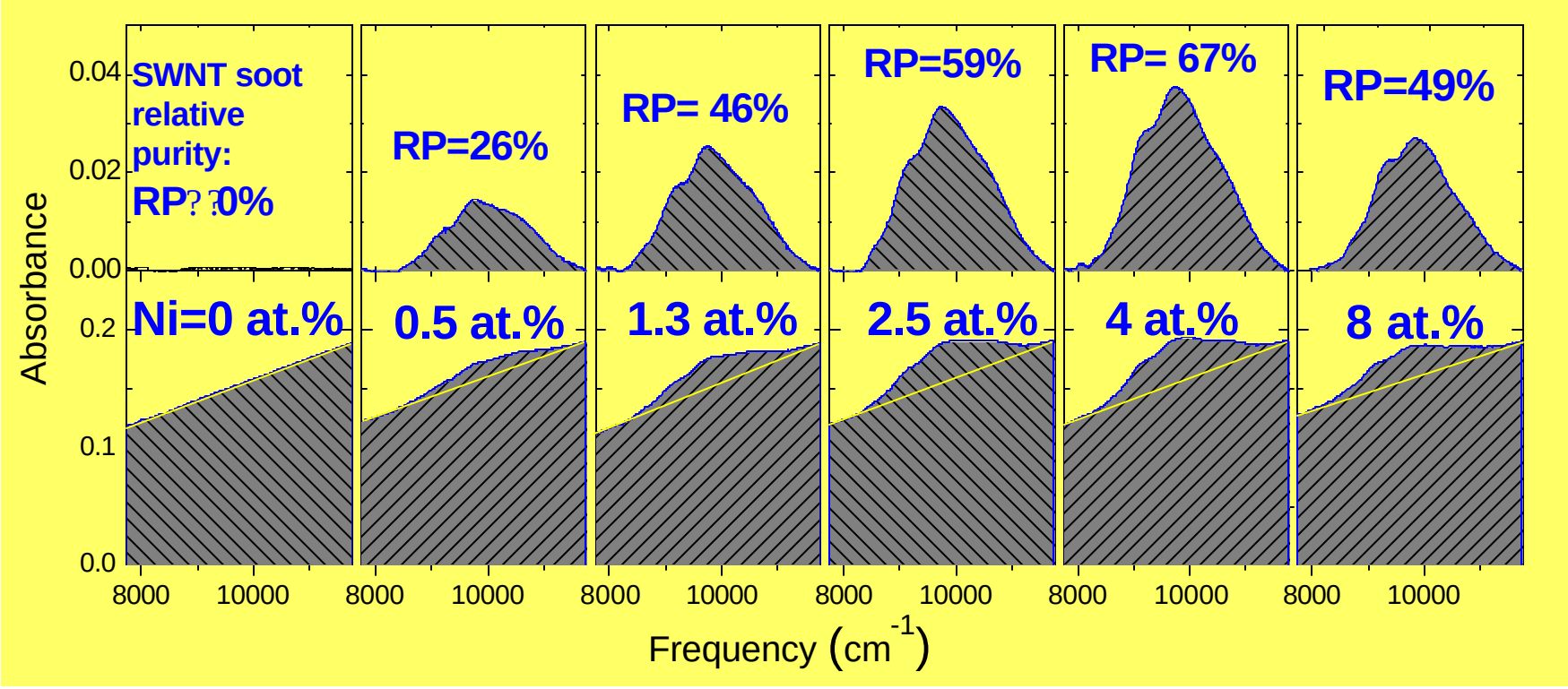
3rd step: 1-2 dilution/ultrasonication cycles to obtain non-scattering dispersion (0.01mg/ml - ABS~0.2 at 12,000 cm^{-1})

Itkis et al., *Nano Lett.* 2003, **3,** 309

Applications: Arc-discharge synthesis

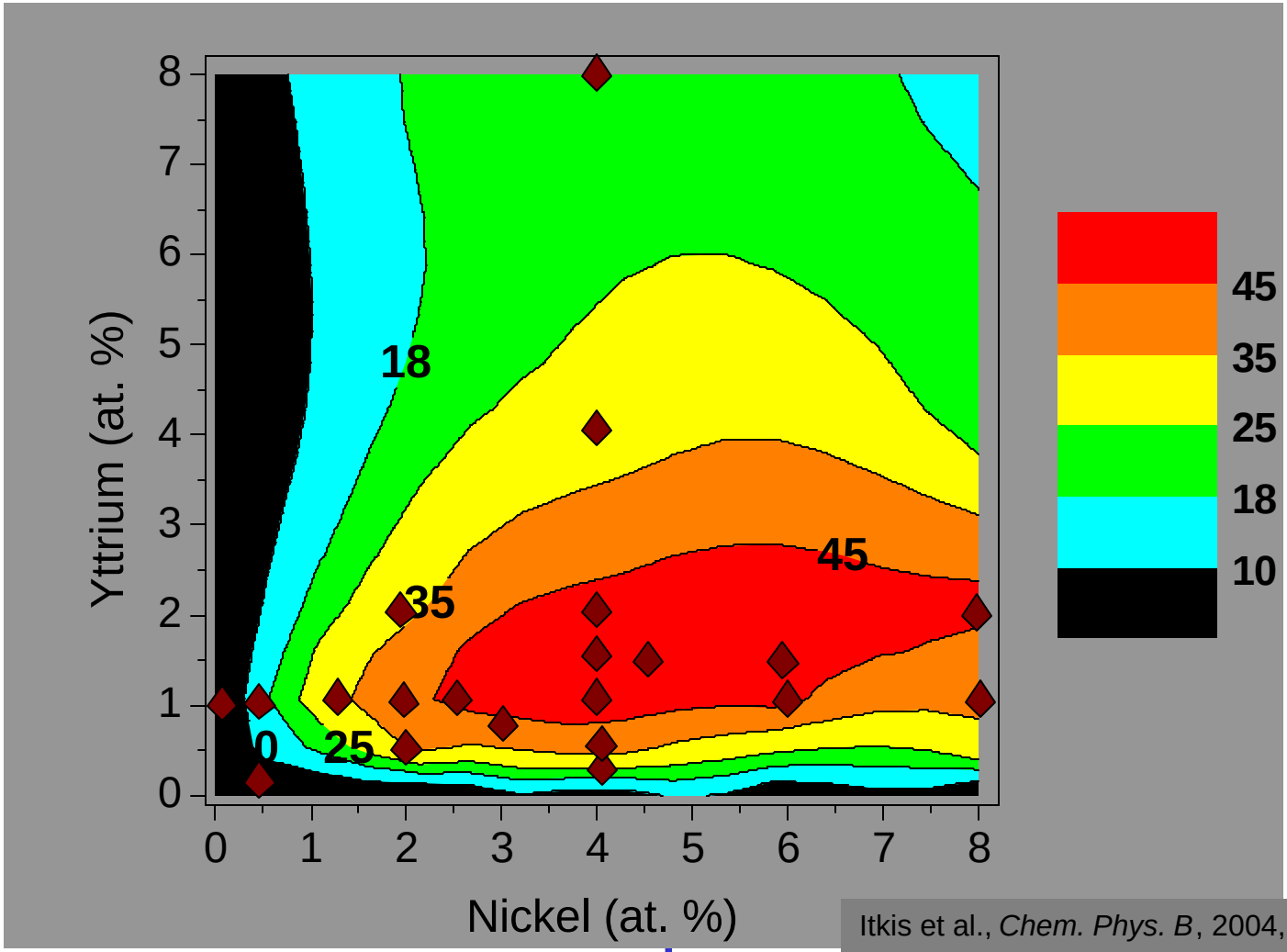
Ni-Y catalyst optimization:

varying Ni, Y=1 at.%



Supports original results by Journet et al., Nature, 1997
Good test for NIR technique

Purity vs. Ni-Y composition:



Itkis et al., *Chem. Phys. B*, 2004, **108**,12770

Using NIR purity evaluation procedure we obtained two-dimensinal contour plot: purity vs Ni-Y catalyst composition

Other well established techniques: TGA and Raman:

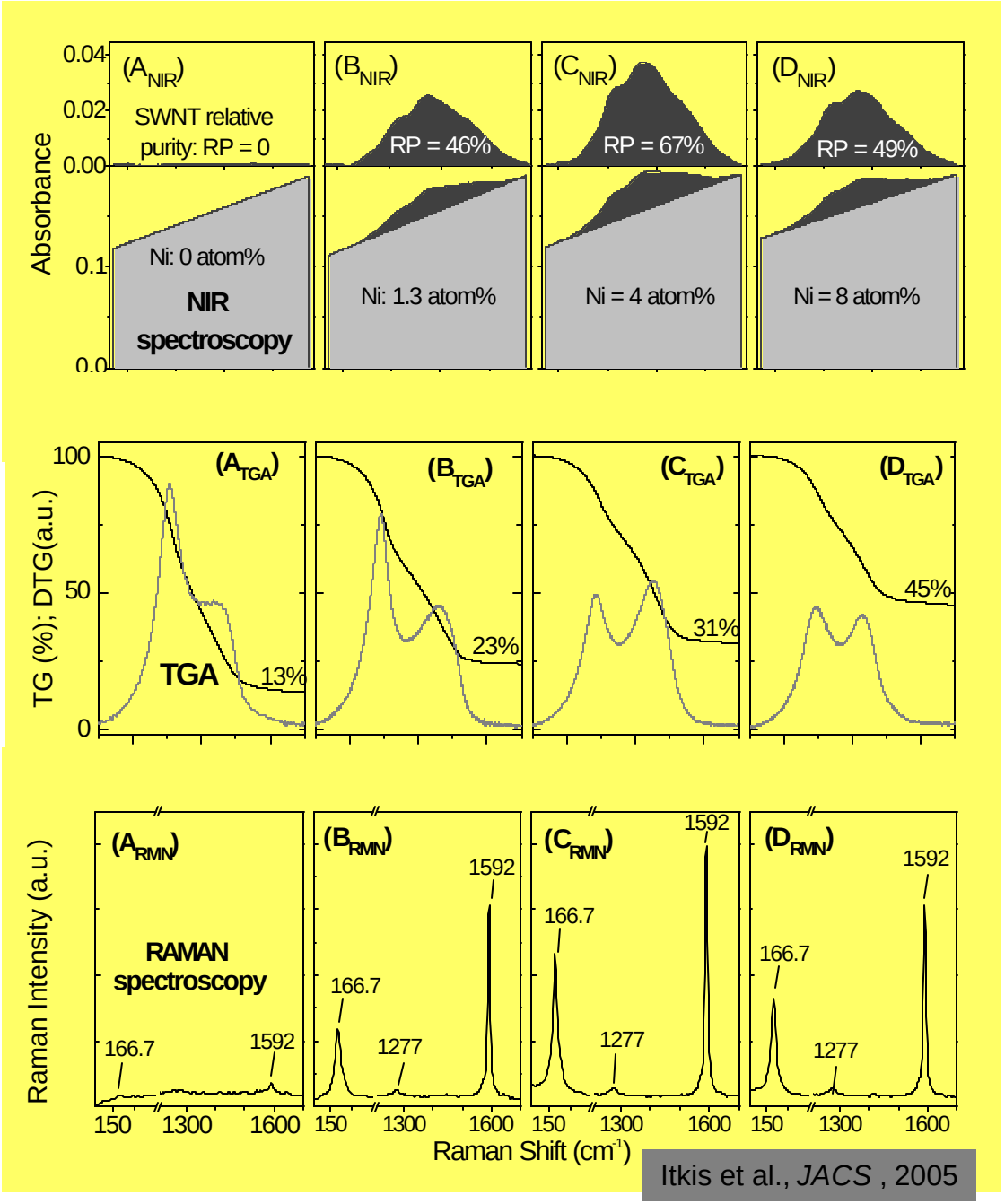
Test NIR against TGA and Raman,

Test Raman and TGA against NIR

Is there any correlation between
NIR, Raman and TGA data?

How efficient are those techniques
for SWNT purity evaluation?

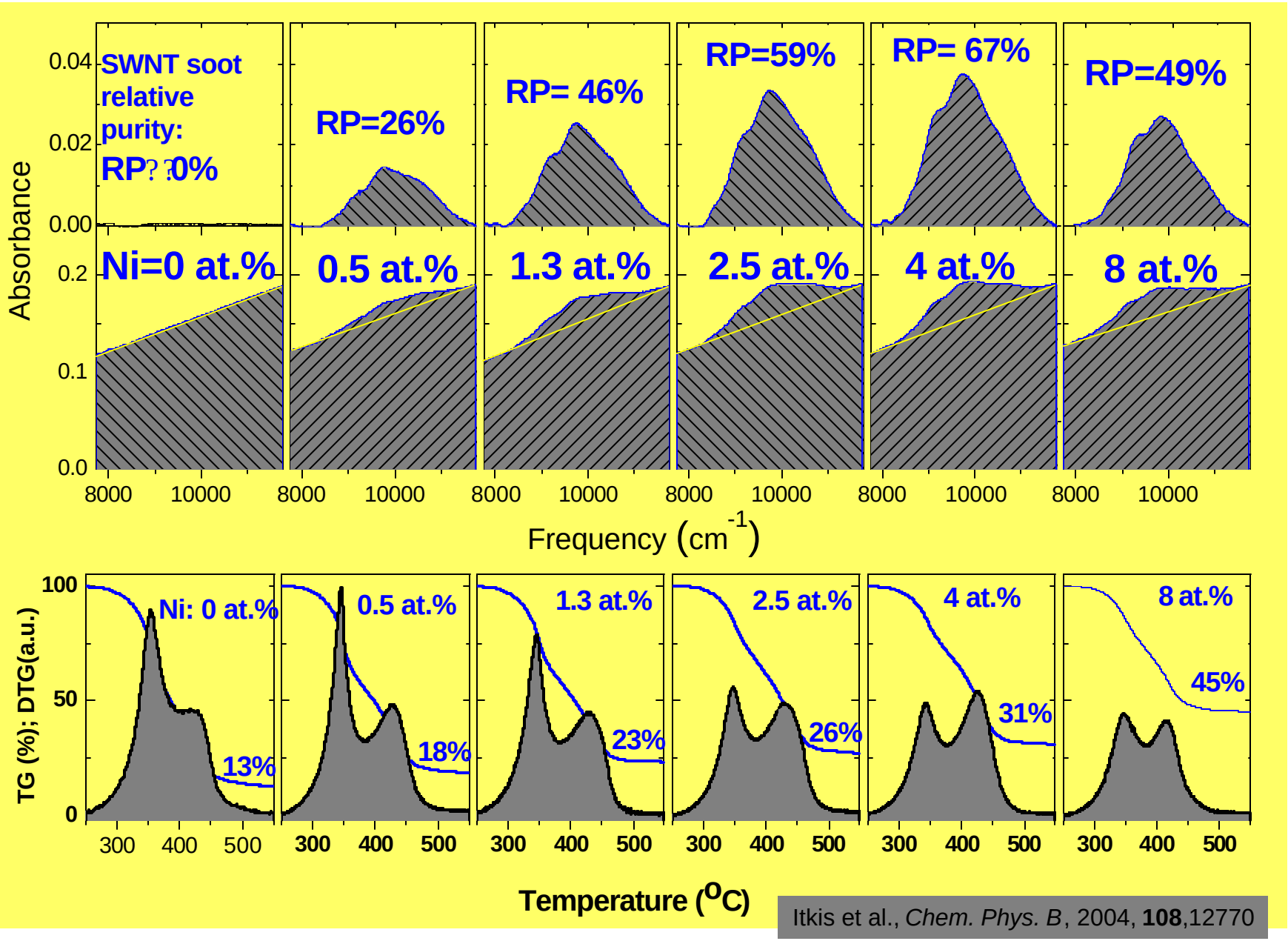
Comparison of NIR, TGA and Raman



Itkis et al., *JACS* , 2005

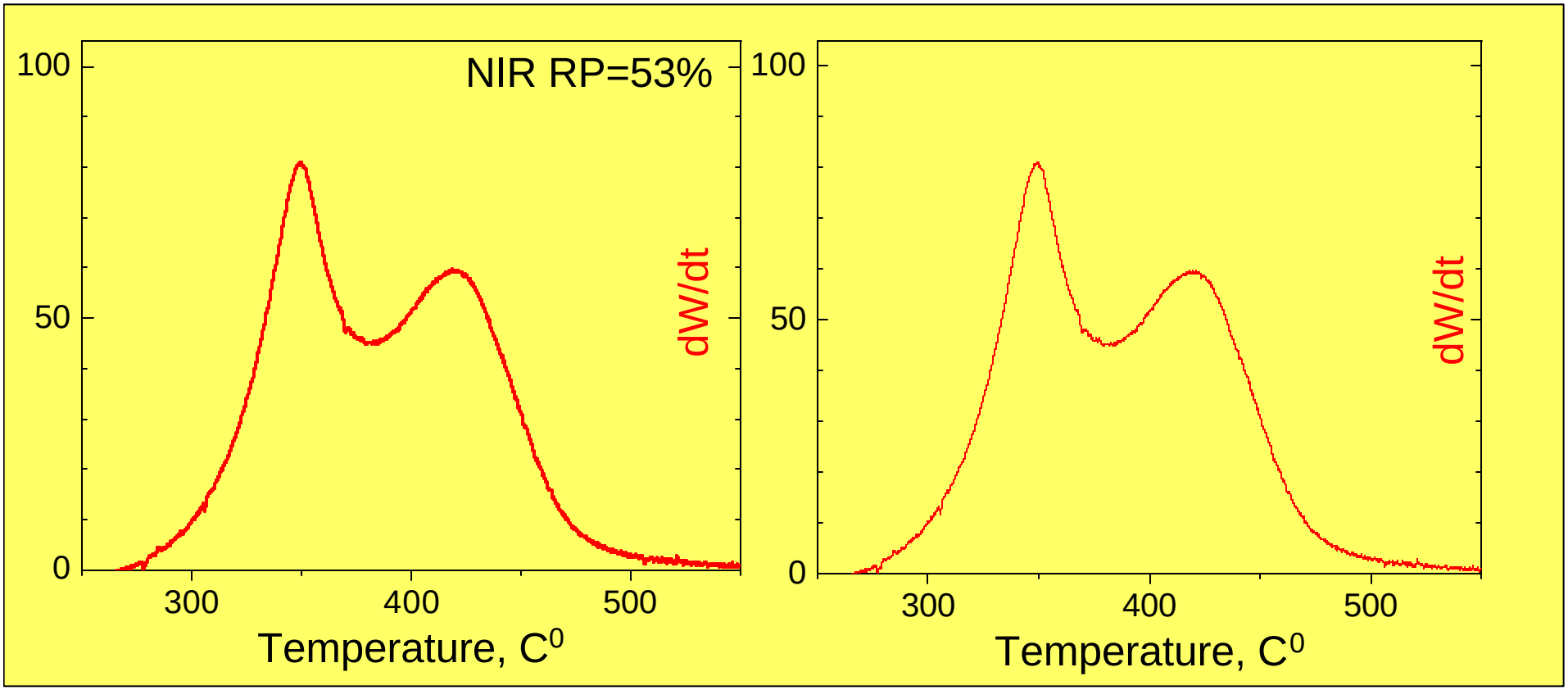
There is a significant degree of correlation between NIR, TGA and Raman data

Correlation of NIR and TGA: Varying Ni, Y=1 at.%



Itkis et al., *Chem. Phys. B*, 2004, **108**,12770

Can we quantitatively extract individual contributions of SWNTs and carbonaceous impurities?

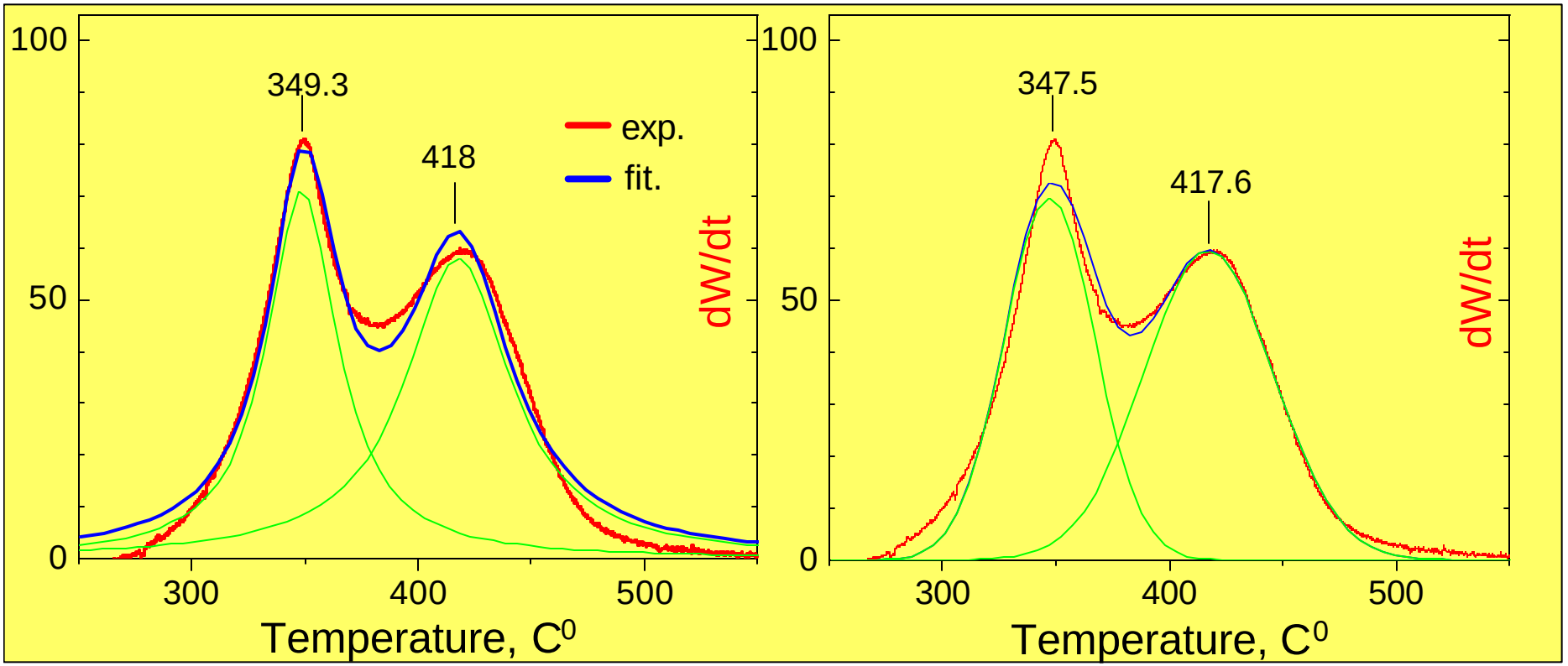


Lorentzian:

$y = (2*A/?)*(w/(4*(x-x_c)^2 + w^2))$

Gaussian:

$y= (A/(w*sqrt(?/2)))*exp(-2*((x-xc)/w)^2)$



Xc1	349.27941	Xc2	417.98779
W1	37.96542	W2	56.53516
A1	4255.13802	A2	5154.9674

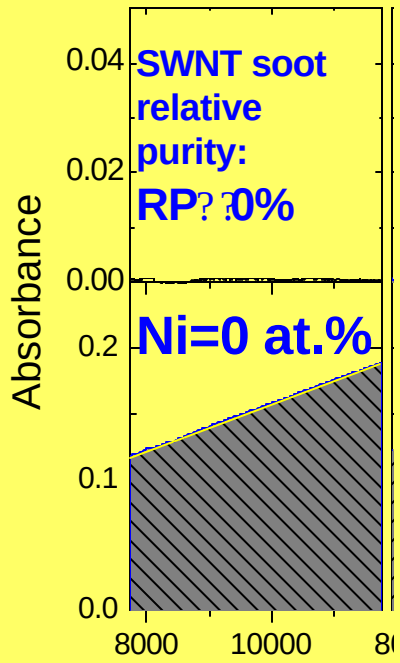
Xc1	347.4	Xc2	417.6
W1	40.2	W2	57.2
A1	3515	A2	4266

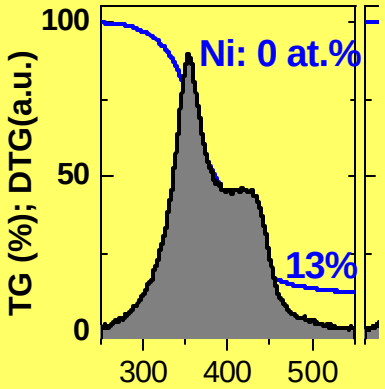
Itkis et al., JACS, 2005

Two components are not enough to obtain a satisfactory fit.

It requires at least four components with no clear physical meaning.

Near-IR and TGA: Ni=0, Y=1 at.%





TGA is the best analytical tool to determine the amount of metal in SWNT soot.

Problems with TGA:

Sample with no SWNTs shows characteristic SWNT-like peak at 420^{o}C

In TGA experiments the AP-SWNT soot behaves as a heterogeneous mixture of unresolved multiple components with a wide distribution of combustion temperatures.

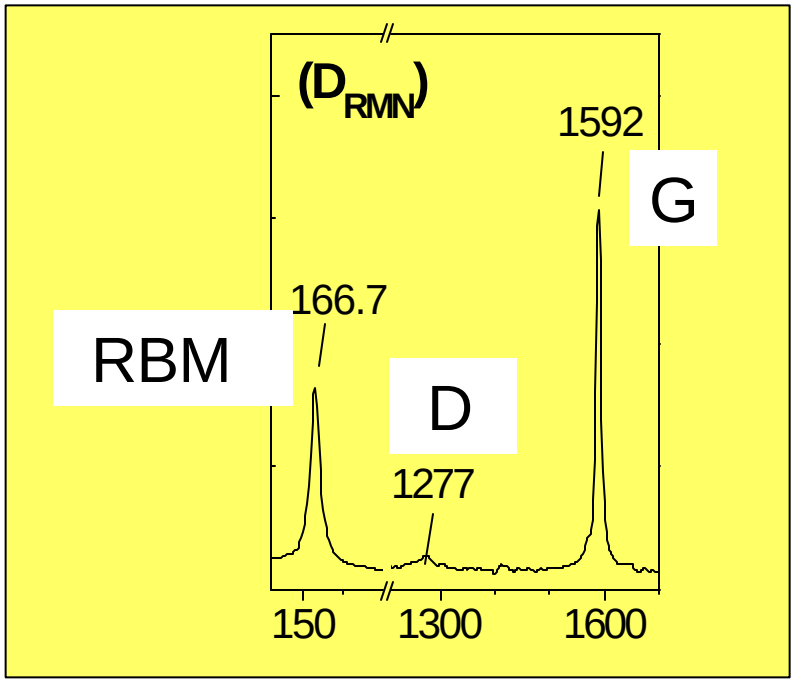
Other complications: exothermic oxidation reaction and dependence on the temperature ramp rate.

Comparison of NIR and Raman spectroscopy for SWNT purity evaluation

Choice of “Raman metric of purity”

Limitations of both techniques

Purity evaluation using Raman spectroscopy



Candidates for Raman-based metric of purity:

- area or amplitude of RB-band
- area or amplitude of G-band
- ratio of amplitudes or areas of G to D bands
- width of D-band (Dillon)

Solution phase Raman spectroscopy produces more reproducible results for evaluation of bulk SWNT samples.

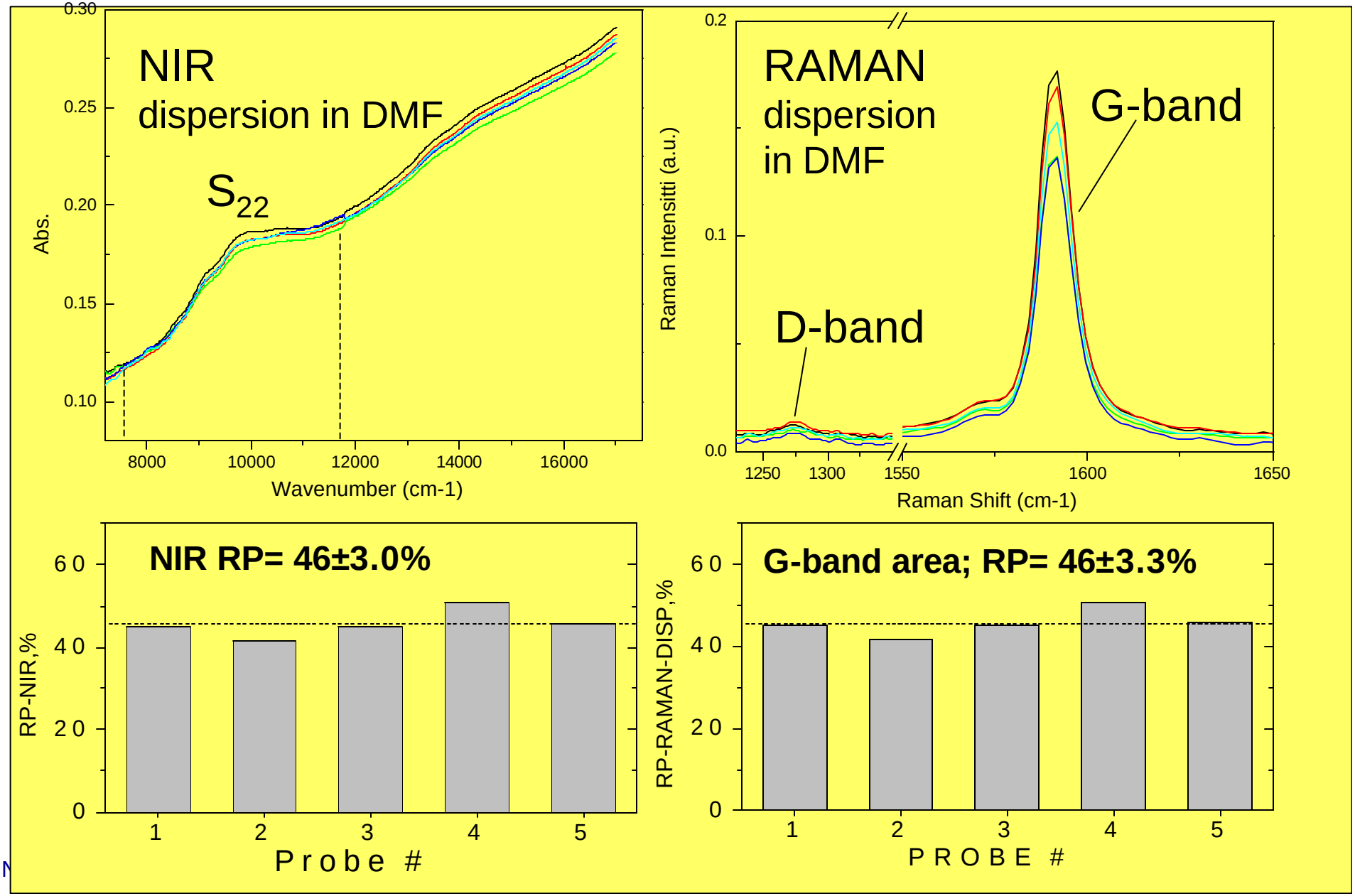
Itkis et al., JACS, 2005

Choice: Solid state or solution phase Raman spectroscopy?

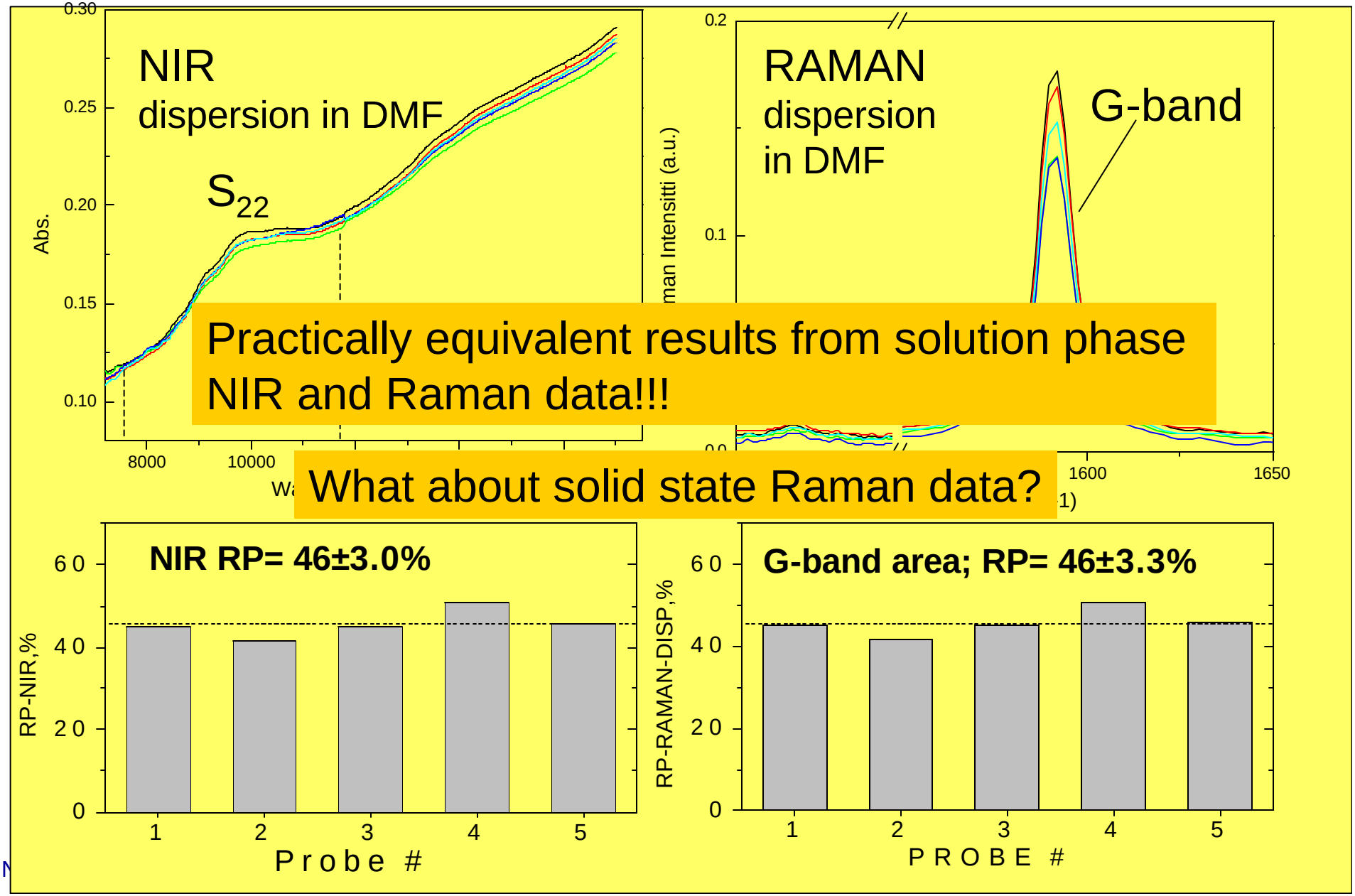
How to compare the reproducibility of NIR and Raman results ?

Experiment:
10g AP-SWNT batch,
5 probe samples of 50 mg each, dispersions in DMF at 0.01 mg/mL
Solution phase NIR and Raman spectra (1064 nm)
Experiment for powder samples: 5 probe powder samples of 50 mg each

Reproducibility of NIR and Raman results for bulk SWNT samples



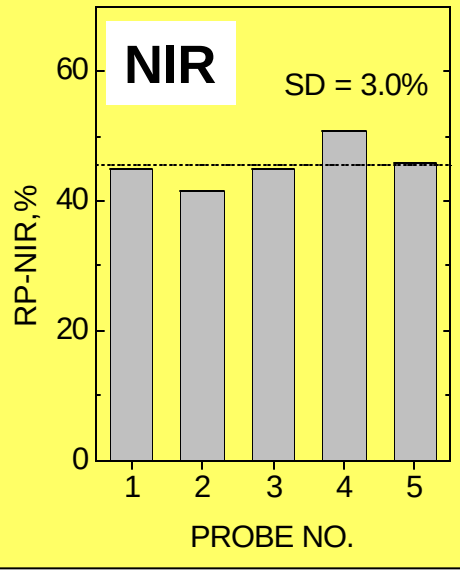
Reproducibility of NIR and Raman results for bulk SWNT samples



Comparison of powder and solution phase NIR and Raman

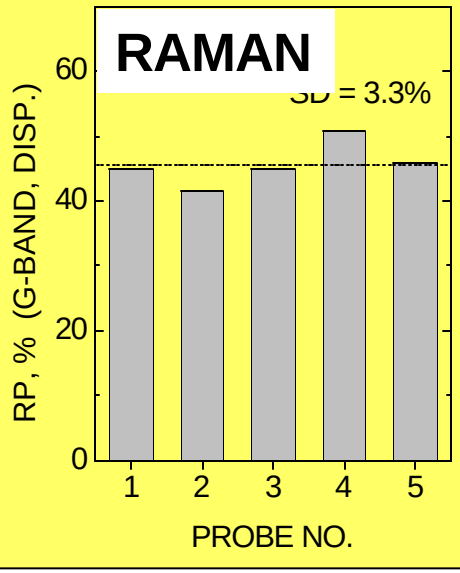
10g batch of AP-SWNTs: five 50 mg probe samples

Dispersion



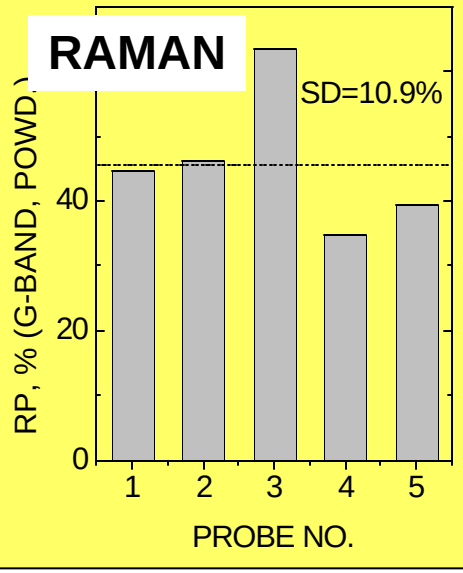
NIR RP= 46±3.0%

G-band area Dispersion



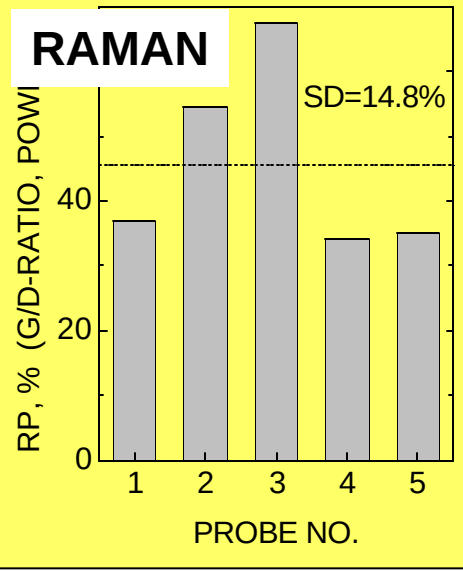
RP= 46±3.3%

G-band area Powder



RP= 46±11%

Ratio: G-band/D-band Powder

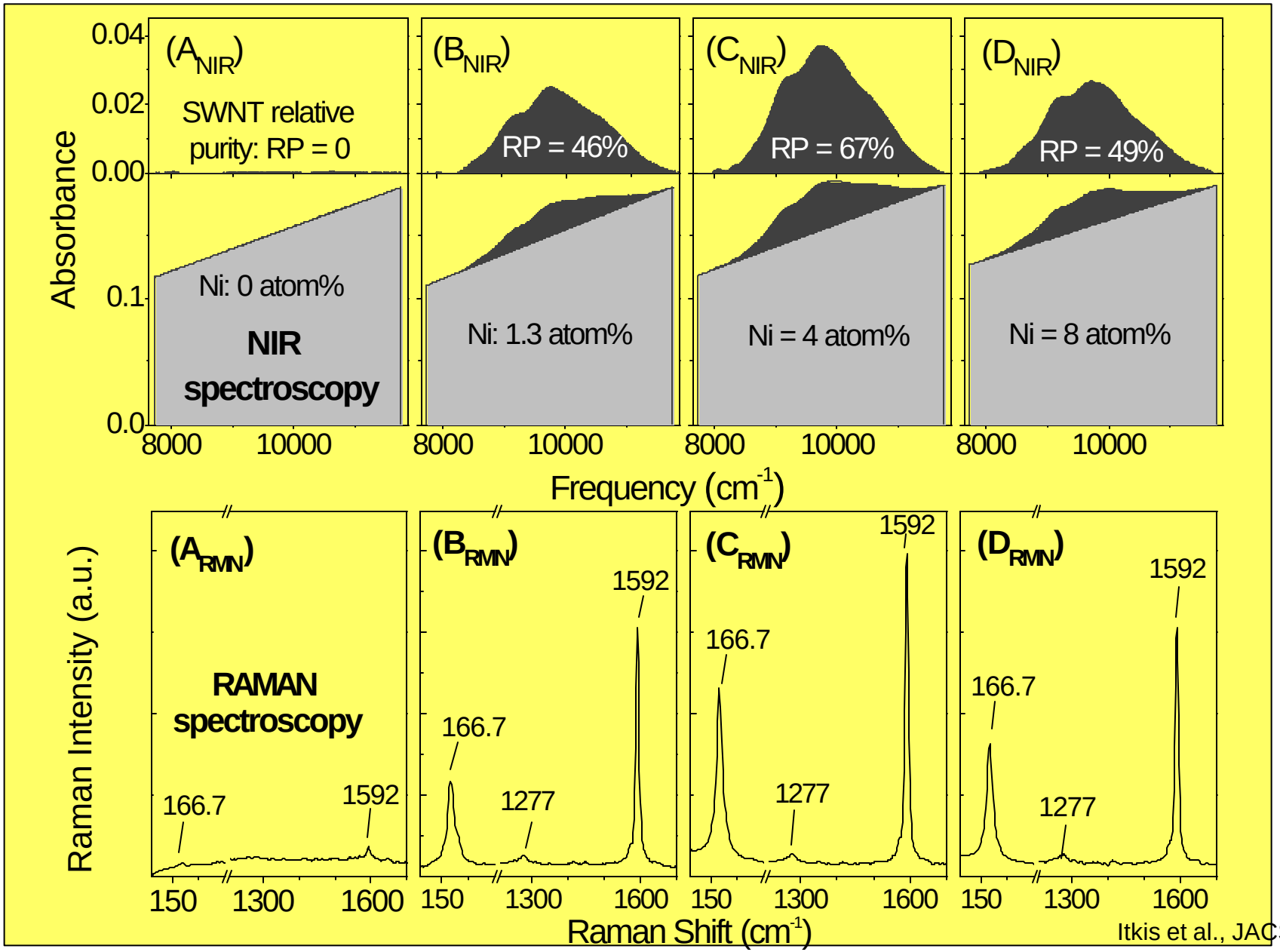


RP= 46±15%

Conclusions:
Solution phase - reproducible results for Raman and NIR spectroscopy.
Raman data for powder show much more scattering.

Itkis et al., JACS, 2005

NIR and Raman spectroscopy – correlation!?



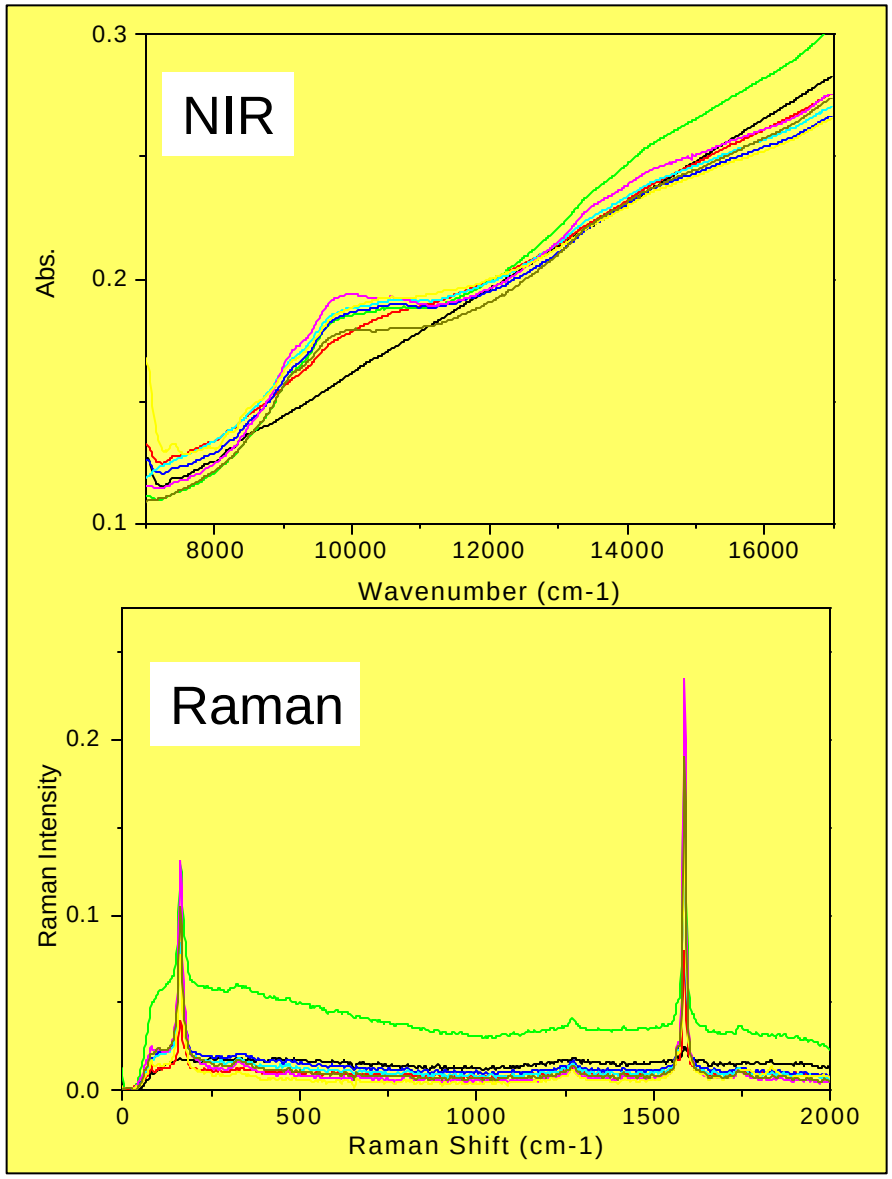
Itkis et al., JACS, 2005

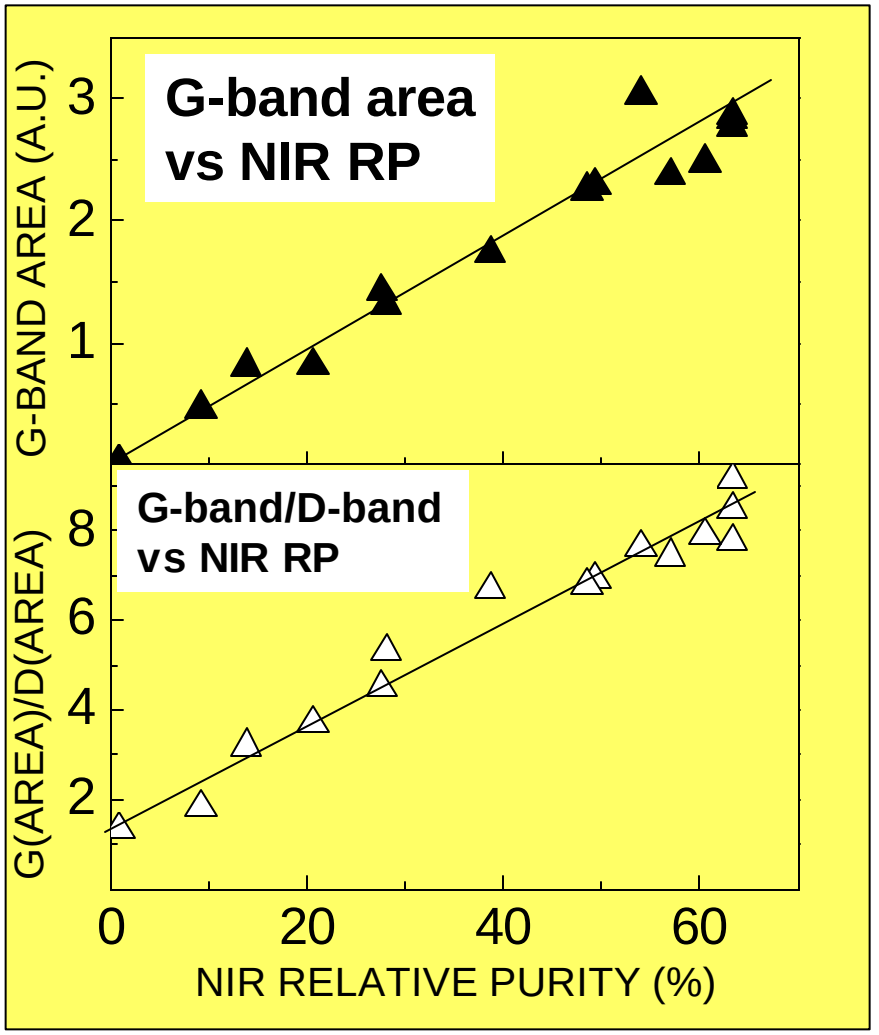
Correlation between NIR and Raman metrics of purity

Experiment:
15 SWNT samples of different NIR relative purity from 0 to 65%
Dispersions in DMF of the same optical density 0.02 at 11760 cm^{-1}
Solution phase NIR and Raman spectra

Correlation between NIR and Raman metrics of purities

15 SWNT samples of different purity, Solution phase NIR and Raman spectroscopy



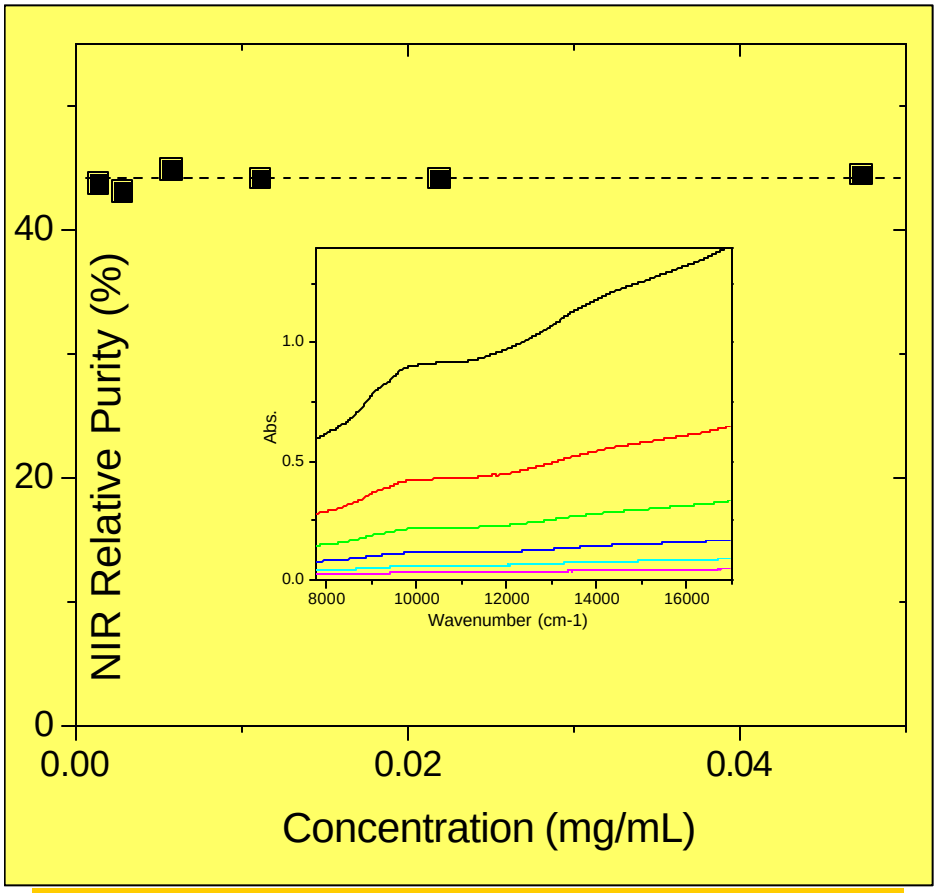


Direct proportionality between NIR and Raman metrics of purity!

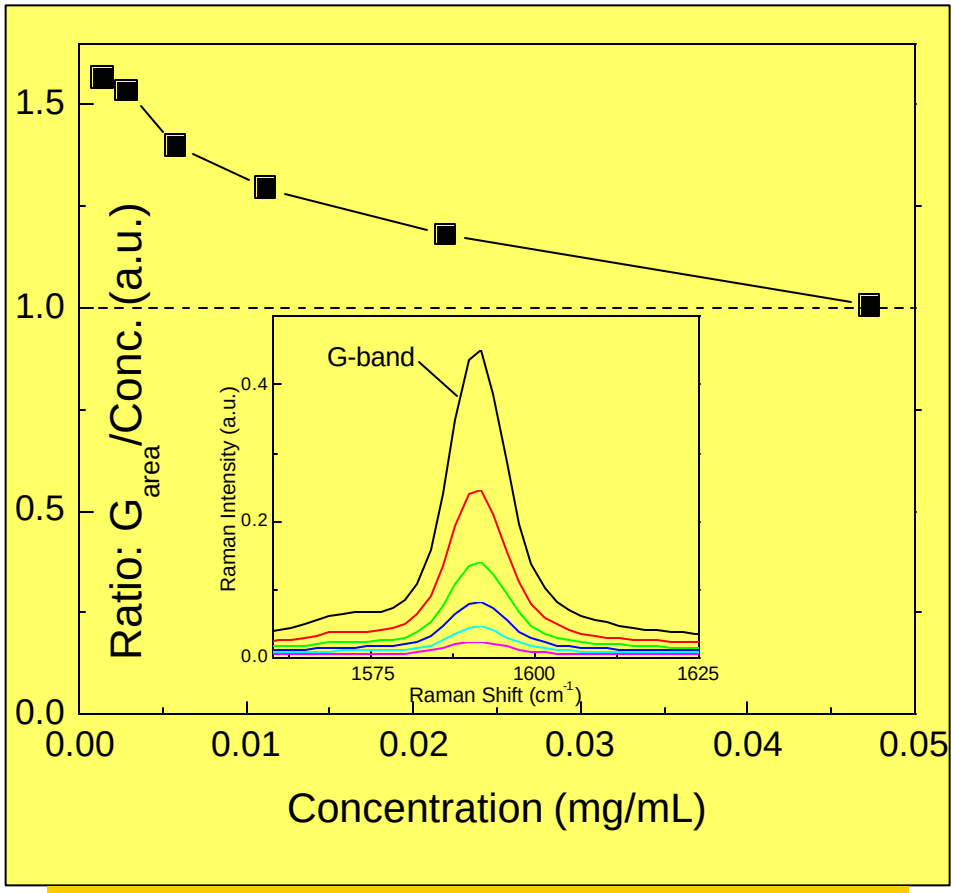
Concentration dependence of NIR and Raman purity metrics

Series of 2-fold dilutions

Solution phase NIR purity vs concentration



Solution phase Raman G-band area vs concentration



NIR does not need exact matching of concentrations

Raman does need exact matching of concentrations

Potential problems with NIR

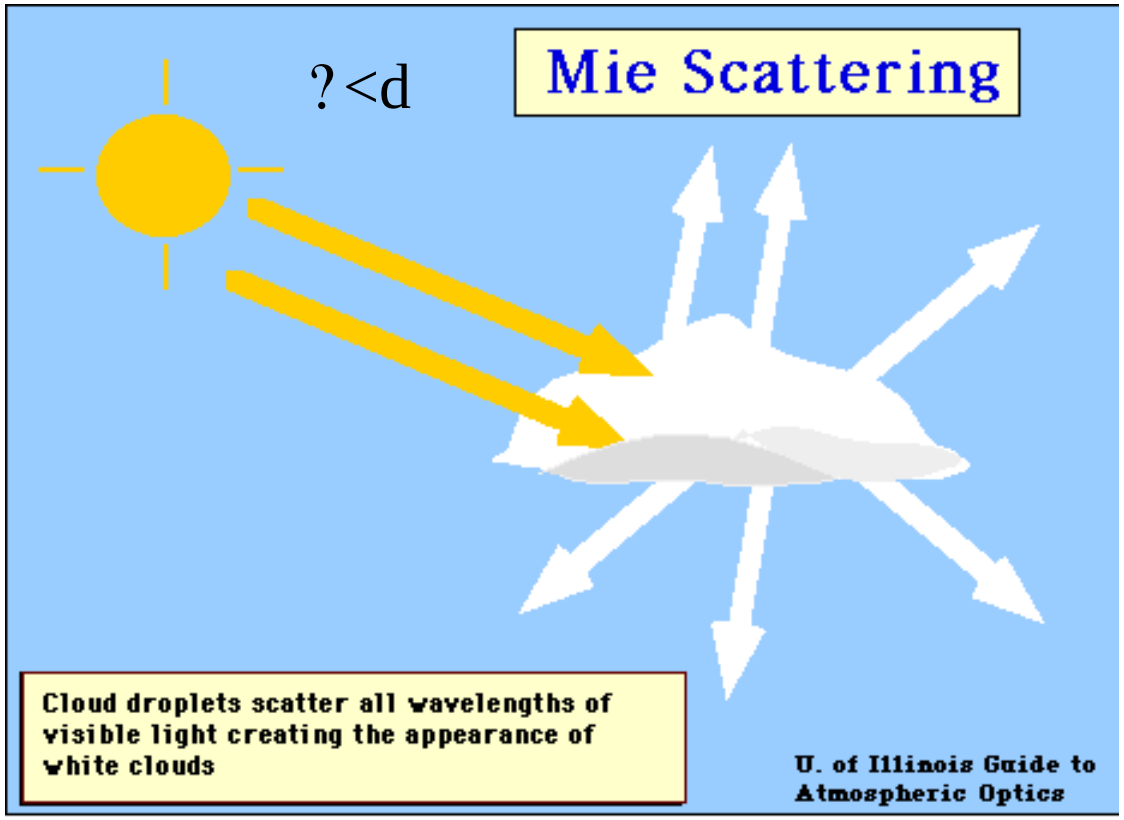
- Light Scattering;
- Influence of doping;
- We do not know absolute purity – only relative purity (work in progress)
- We can not evaluate SWNT materials with a wide distribution of diameters (for example CVD)
- How to compare SWNTs with different diameter distribution? (work in progress)

Some simplifications:

- We are using the simplest approach - linear baseline subtraction in order to avoid introduction of multiple fitting parameters;
- We assume equal per-carbon extinction coefficient for SWNTs and carbonaceous impurities (averaged over spectral range).

Light Scattering

Rayleigh scattering:? >d; from atmospheric gases – air molecules



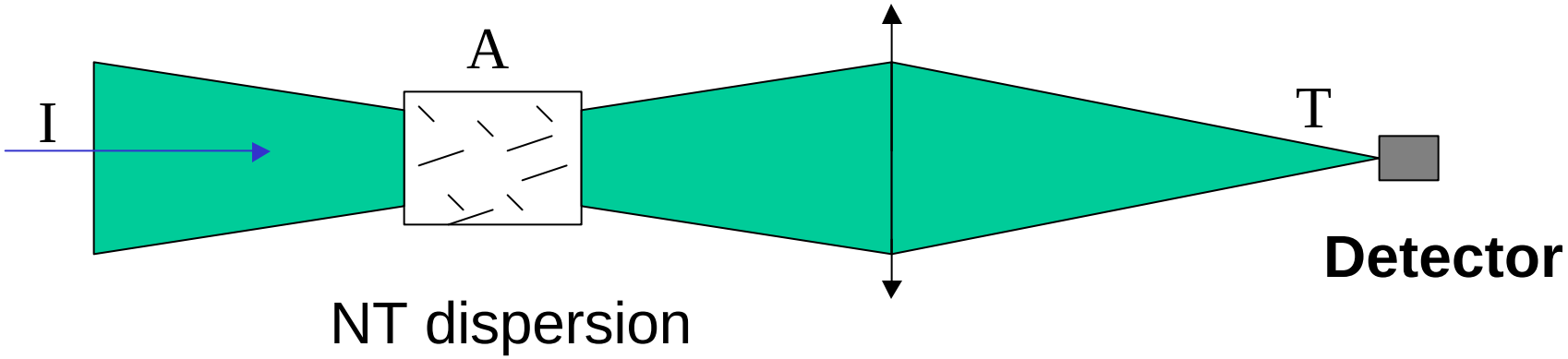
In UV-Vis-Near-IR We have a crossover between SWNT length and wavelength of incident light

Influence of Scattering on Purity evaluation

Detector Sees:

Transmittance(T) = Incident(I) – Absorbance(A); $T = I - A$;

A= I –T

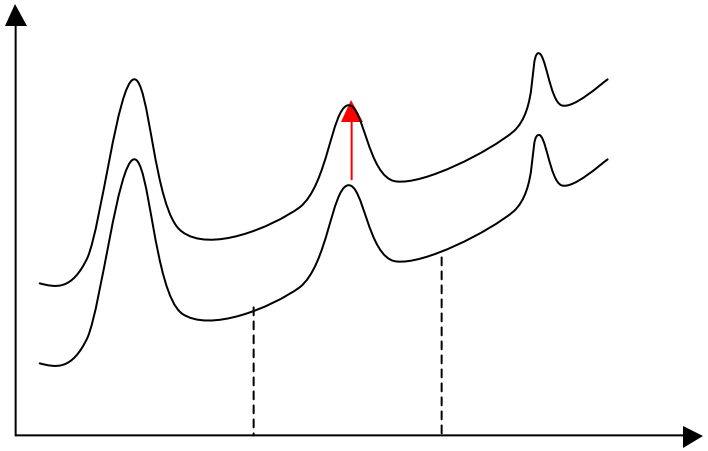


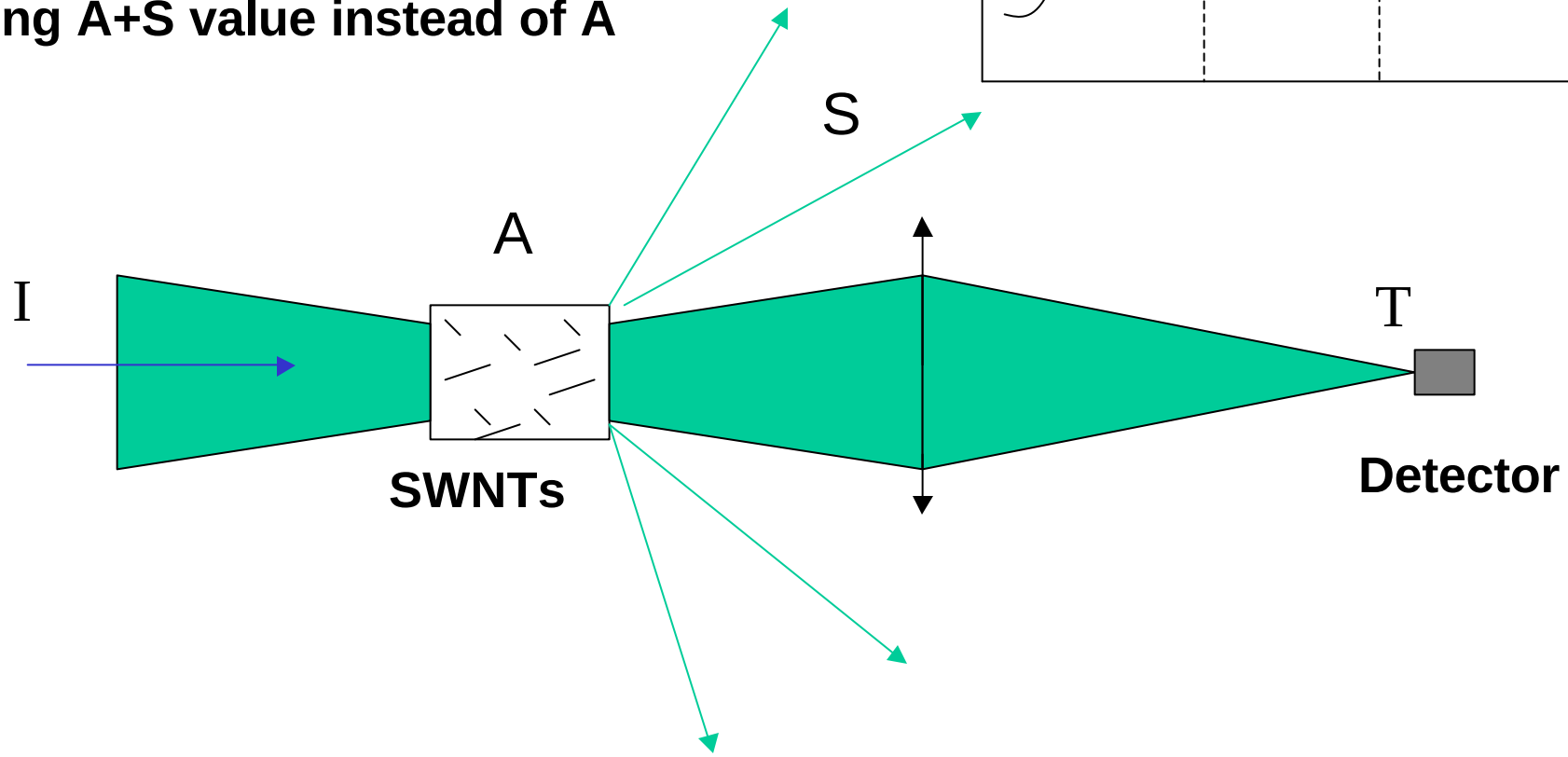
Assumption - no scattering

Contribution of scattering to purity evaluation (raising the baseline)

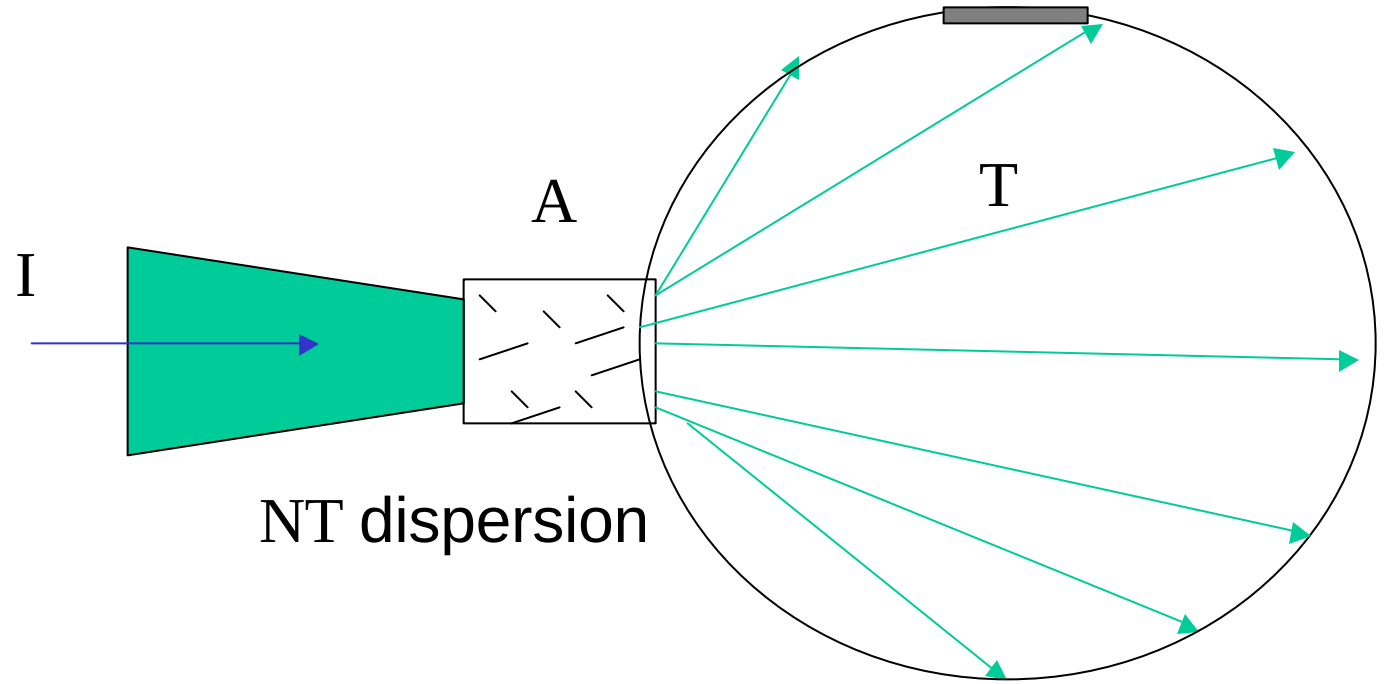
In case of scattering: T = I – (A + S)

Scattering shows up as an extra absorption with no SWNT features, just raises baseline, which would reduce measured purity. From transmission measurements we are getting A+S value instead of A

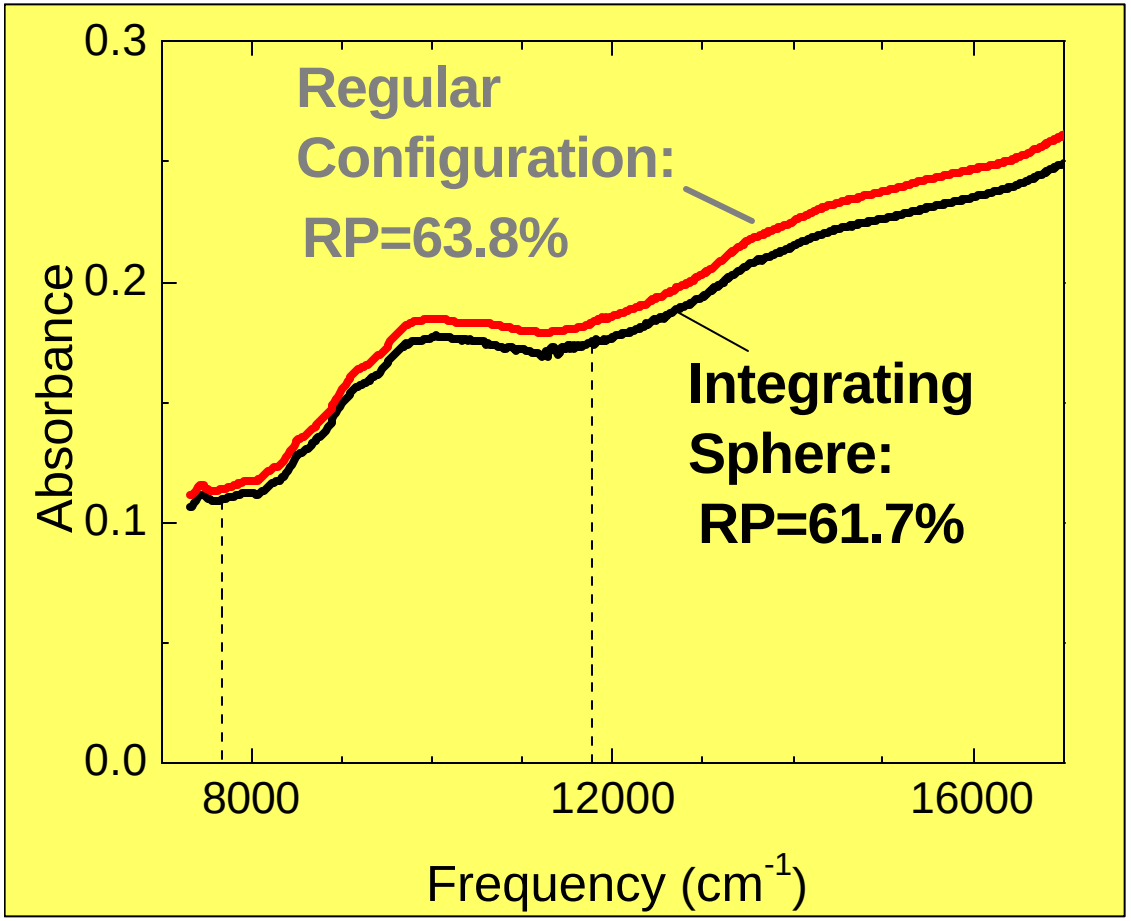




Integrating Sphere



Purity in Regular and in Integrating Sphere Configuration



	NIR relative purity, regular config.	NIR relative purity integr. sphere
#1	20.5%	16.5%
#2	63.8%	61.7%
#3	38.5%	35.5%

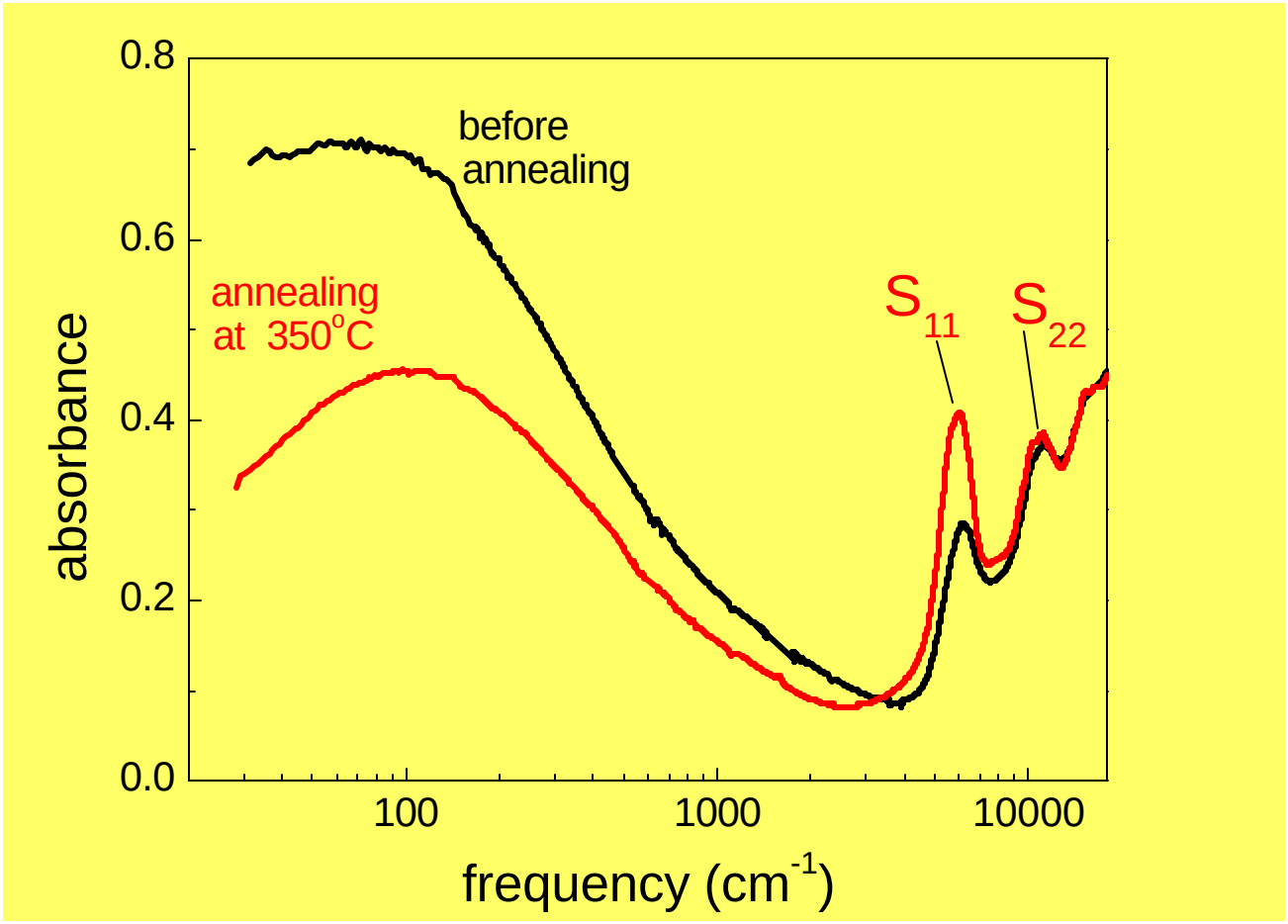
Conclusion: Scattering does not affect NIR purity evaluation if a proper sample preparation protocol is followed

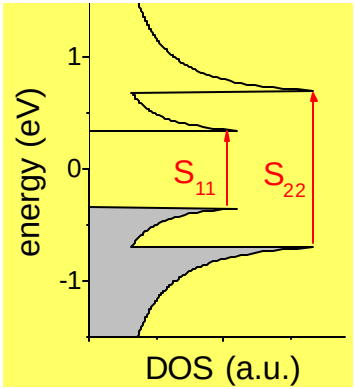
Itkis et al., JACS, 2005

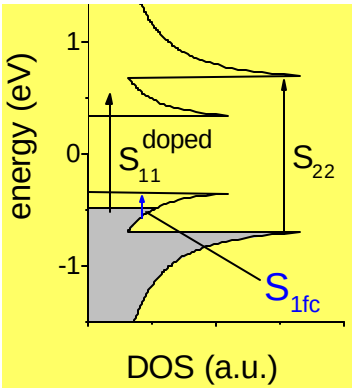
Evaluation of purified or chemically modified SWNTs by NIR and Raman spectroscopy.

Effect of doping

Effect of doping and de-doping on S_{11} and S_{22} interband transitions. Purified SWNTs before and after annealing



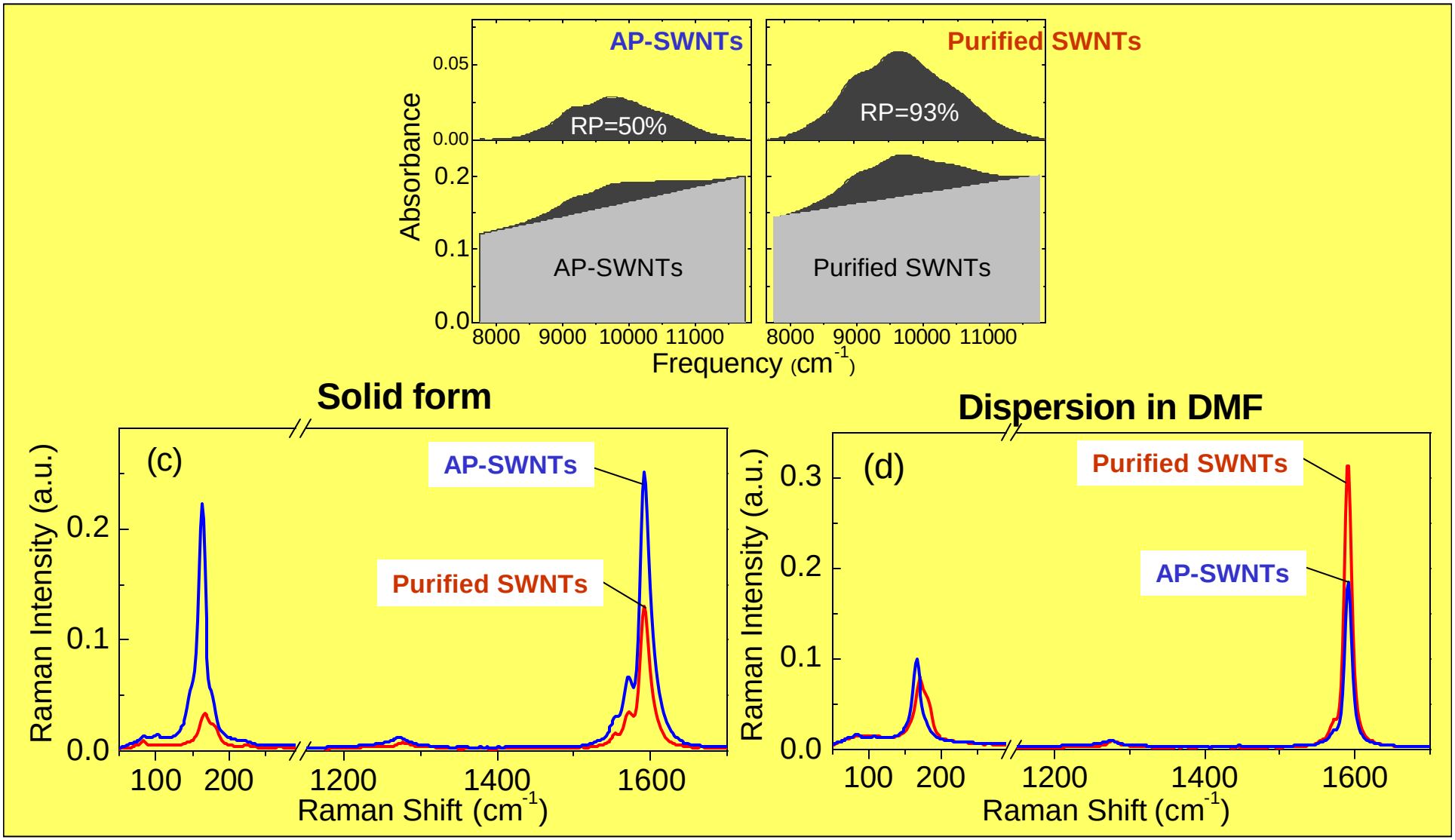




2nd interband transition is not strongly affected at moderate levels of doping;
+ de-doping effect of DMF for solution phase NIR

Itkis et al., *Nano Lett.* **2002**, 2, 155

Specifics of evaluation of purified SWNTs by NIR and Raman spectroscopy



Solid state Raman signal is suppressed in purified SWNTs, unless the final step is vacuum annealing. DMF facilitates de-doping in solution phase.

Itkis et al., JACS, 2005

Comparison of purity of SWNTs with different diameter distributions - work in progress

We have data only on relative purity.
How to obtain absolute purity?

Find 100% pure reference sample – work in progress

Conclusions

- Solution phase NIR spectroscopy provides a simple and reliable metric of relative carbonaceous purity for arc and laser ablation produced SWNTs.

- Evaluation of absolute purity can be achieved by producing 100% pure reference samples – joint efforts of the SWNT community

- Multiple characterization technique should be used to confirm 100% pure reference samples

- For evaluation of bulk SWNT quantities appropriate sample preparation/homogenization procedure is important

- Limitation of NIR technique – SWNTs with wide distribution of diameters, such as CVD-SWNTs. HiPco is an intermediate case.

- There is a correlation between NIR, Raman and TGA purity data. Limitations of Raman – resonance character, sensitivity to doping, dependence on concentration. TGA – gives metal fraction, but can not resolve contributions of different carbon-based fractions. (Itkis et al., JACS, 2005 in press)

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